



# Molecular Scale Heavy Element Science

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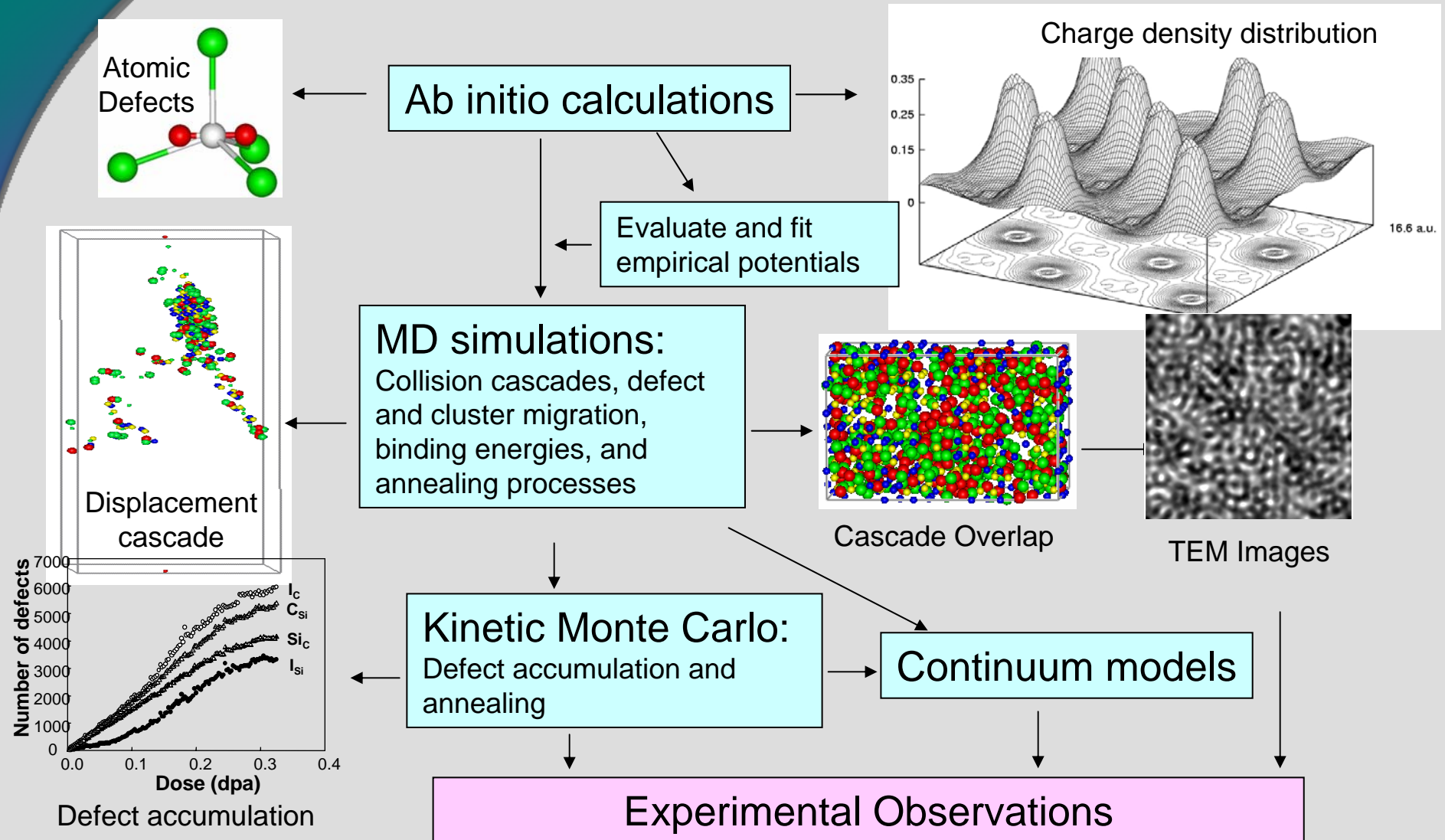
# Molecular scale heavy element simulation is needed for

- ▶ Materials design
  - Fuels
  - Material behavior in hostile environment
  - Long term behavior (repository)
  - Understand macroscopic behavior
  - Sensors
- ▶ Dissolution process
  - Improved transuranic dissolution
- ▶ Separation process
  - Efficient
  - Environmentally clean
  - “chemical reversibility”

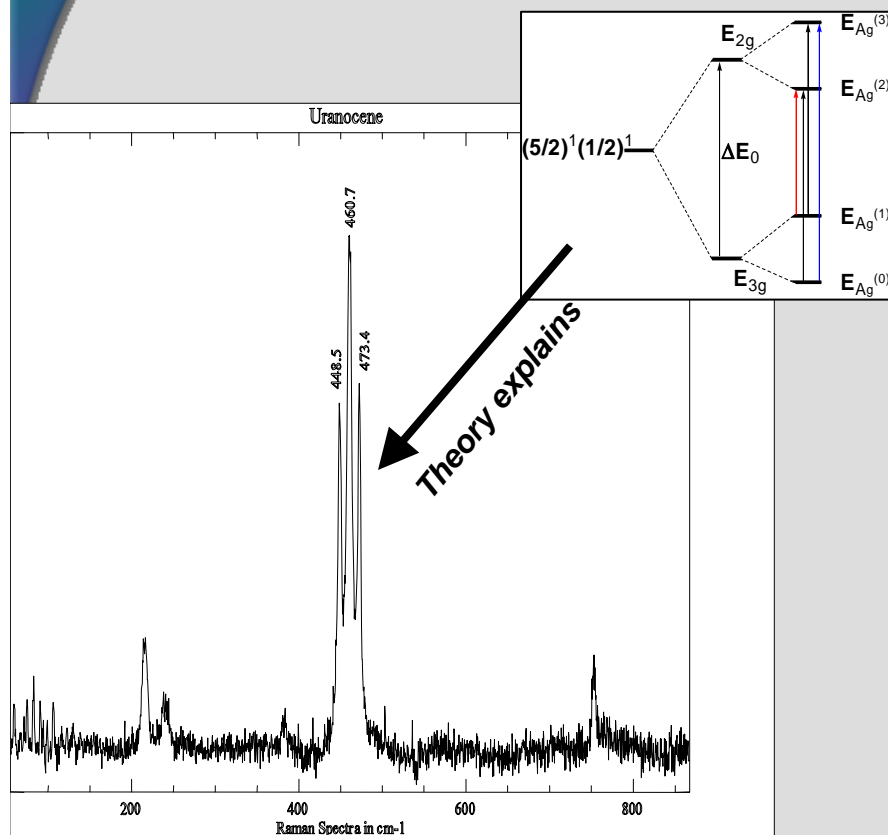
## Some of the computational challenges

- ▶ Multiscale nature in spatial and temporal dimensions – interesting physics, mathematics and computer science challenges
- ▶ Interfacial reactions
- ▶ Solution phase reactions
- ▶ Heavy elements – especially open shells
- ▶ Determining appropriate oxidation state
- ▶ Limited experimental data for benchmarking
- ▶ Dynamics

# Multi-Scale Modeling of SiC



# Modeling and Interpreting Spectroscopic Properties in Actinide Complexes



## Uranocene Research:

- ▶ High-resolution Raman spectroscopy experiments observed structure in broad electronic resonance band
- ▶ 460 cm<sup>-1</sup> band is found to have fine structure of three distinct bands
- ▶ Computational modeling used to assign and interpret vibrational Raman spectra
- ▶ Calculations show that fine structure is due to spin-orbit splitting of both the ground state and first excited state

## Collaborative Research

Modeling: Jun Li (EMSL@PNNL)

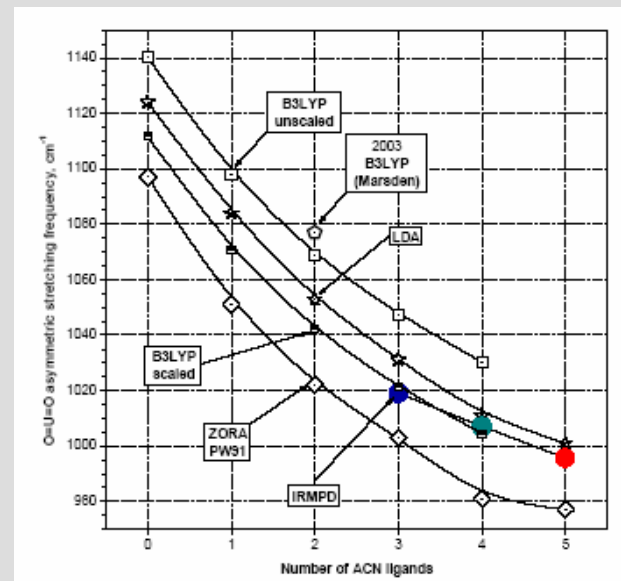
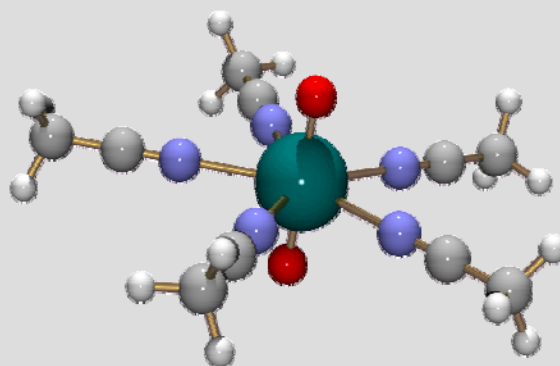
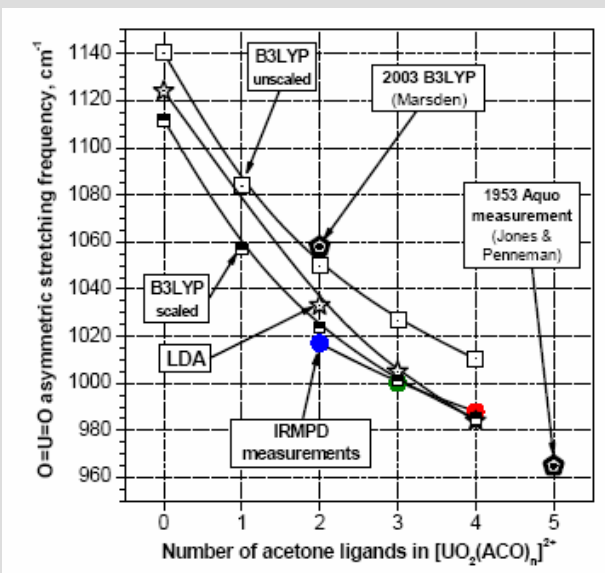
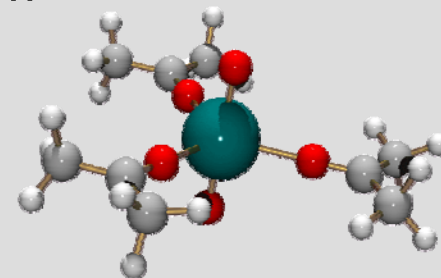
Experiments: Robert Compton (U. Tennessee)

# Gas-phase IR spectra of $\text{UO}_2^{2+}$ and $[\text{CeOH}]^{2+}$ complexes

- ▶ Very exciting experimental data, at least for computational actinide chemistry
  - Gas-phase: no environmental effects to worry about
  - Benchmark for computational methods
- ▶ Collaboration with experimentalists:
  - Groenewold, Gianotto, Cossel, *Idaho National Laboratory*
  - Van Stipdonk, *Wichita State University*
  - Oomens, Polfer, Moore, *FOM Instituut voor Plasmafysica, The Netherlands*
  - For uranyl, modeling in collaboration with Visscher, *Vrije Universiteit Amsterdam, The Netherlands*

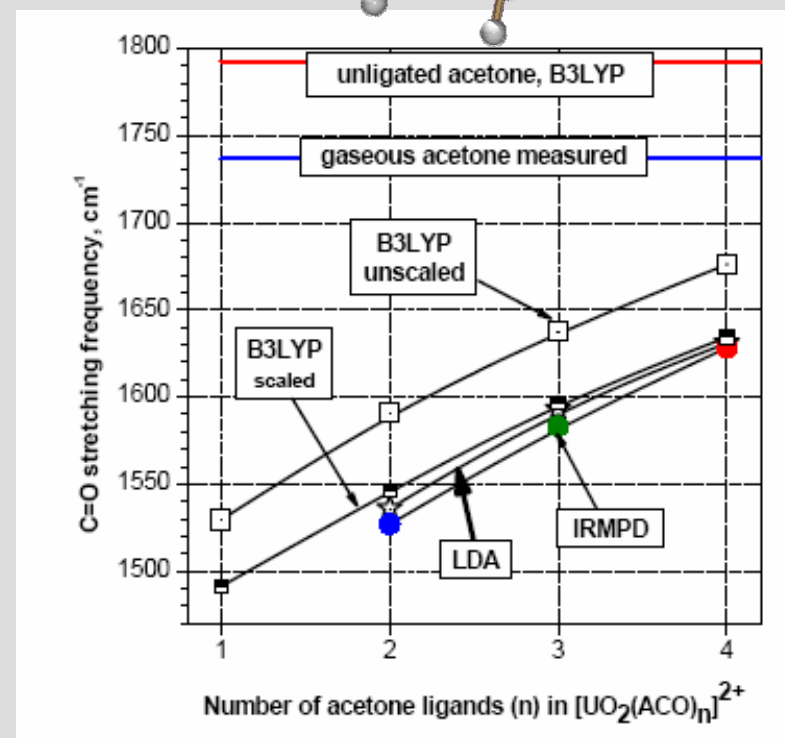
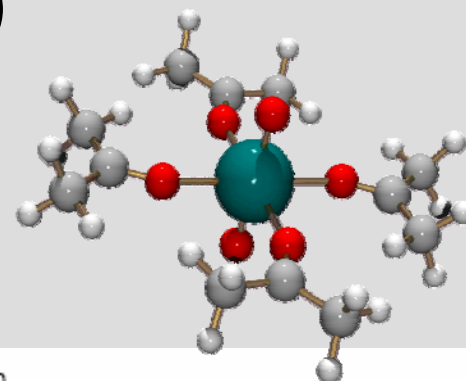
# UO<sub>2</sub><sup>2+</sup> with acetone or acetonitrile

- ▶ Carbon and carbonyl oxygen coplanar with uranium
- ▶ Uranyl asymmetric stretch red shifted
  - Shifted further as more ligands are added
- ▶ Acetone stronger nucleophile than acetonitrile
- ▶ Uranyl with 5 waters (in solution) lower than acetone:
  - 4- and 5-water 40 cm<sup>-1</sup> higher than acetone in gas-phase



# $\text{UO}_2^{2+}$ with acetone or acetonitrile (cont.)

- ▶ Similar good agreement between calculated and measured C=O stretch frequencies
- ▶ C=O stretch also red shifted relative to free acetone:
  - Weakening C=O bond
  - Weakening lessens when more ligands are added





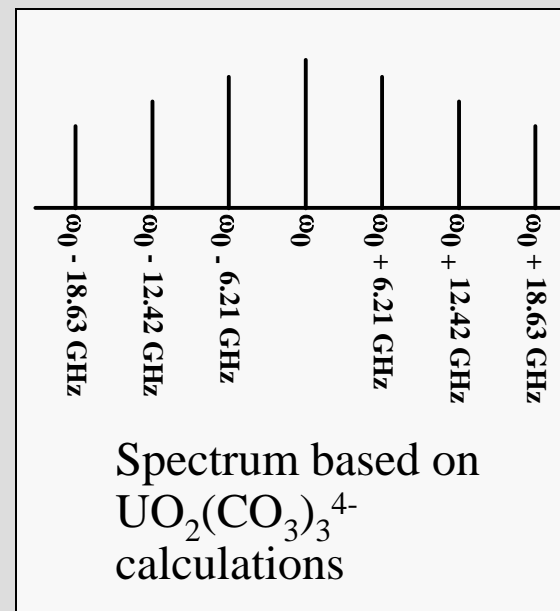
# NMR on Uranyl Complexes: Can we do NMR on uranium atoms?

## ► Calculations show that

- NQCC for  $^{235}\text{U}$  is large (>4 orders of magnitude compared to  $^{17}\text{O}$ )
  - Quadrupolar coupling 3 orders of magnitude larger than Zeeman effect
  - For NMR quadrupolar coupling is perturbation to Zeeman effect
- Nuclear transition energies in the GHz range

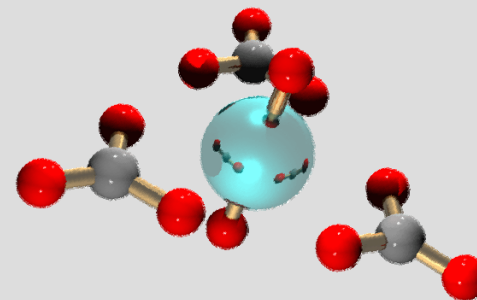
## ► Makes NMR measurements impractical

- Can be studied using Nuclear Quadrupole Resonance, but we need to calculate transitions very accurately !



# NMR on $^{17}\text{O}$ : Does computation give good results?

- ▶ Comparing theory and experiment  
uranyl carbonates in solution

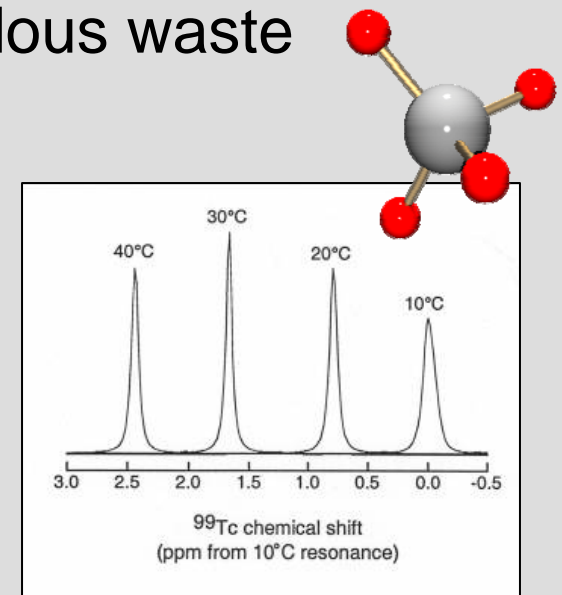


Molecule	$^{17}\text{O}$ location	$\delta_{\text{iso}}$ (calculated)	$\delta_{\text{iso}}$ (experiment)
$\text{UO}_2^{2+}$	$\text{UO}_2$	1160	1121
$\text{UO}_2(\text{CO}_3)_3^{4-}$	$\text{UO}_2$	1050	1098
	$\text{CO}_3$	266, 341	225
$\text{CO}_3^{2-}$	$\text{CO}_3$	209	185

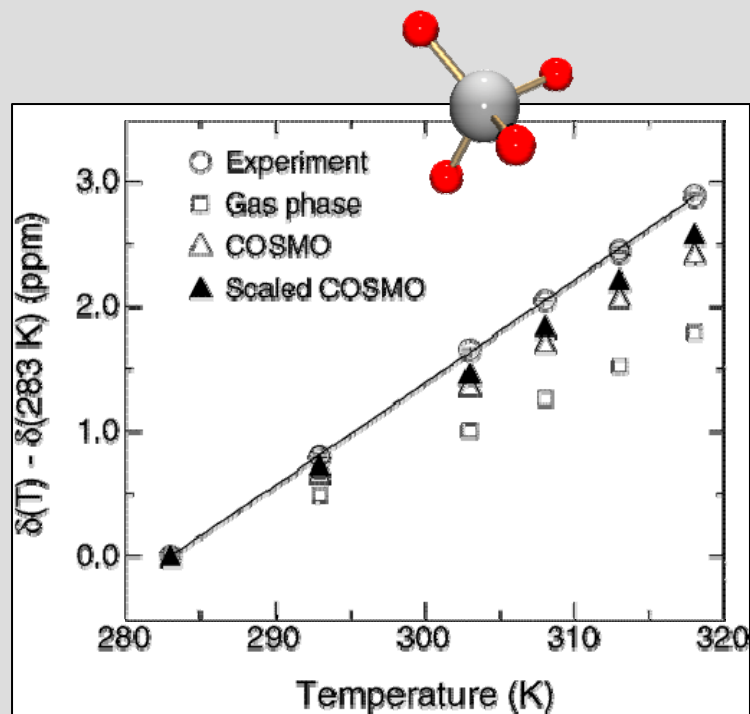
Experiments by Allen et al. (LANL), Inorg. Chem. 34, 4797 (1995)

# NMR on $^{99}\text{Tc}$ in Pertechnetate

- ▶ Pertechnetate ion ( $\text{TcO}_4^-$ ) with Tc(VII) highly soluble
- ▶ Cleanup efforts geared to reducing technetium oxides to insoluble forms
- ▶ NMR could be non-destructive technique to measure pertechnetate remaining in the hazardous waste
  - NMR measurements revealed a temperature and isotope dependence of  $^{99}\text{Tc}$  NMR signal
- ▶ Computational modeling used to provide explanation



# Calculation of $^{99}\text{Tc}$ chemical shift



- Calculation of temperature and isotope dependence
- Both isotope and temperature dependencies are due to vibrational motion
- Temperature dependence:
  - Calculated chemical shifts show the correct trends
  - Dependencies slightly underestimated
- Isotope dependence chemical shift in close agreement with experiment

Results published in the JACS (2004)

## Calculation of $^{99}\text{Tc}$ - $^{17}\text{O}$ spin-spin coupling

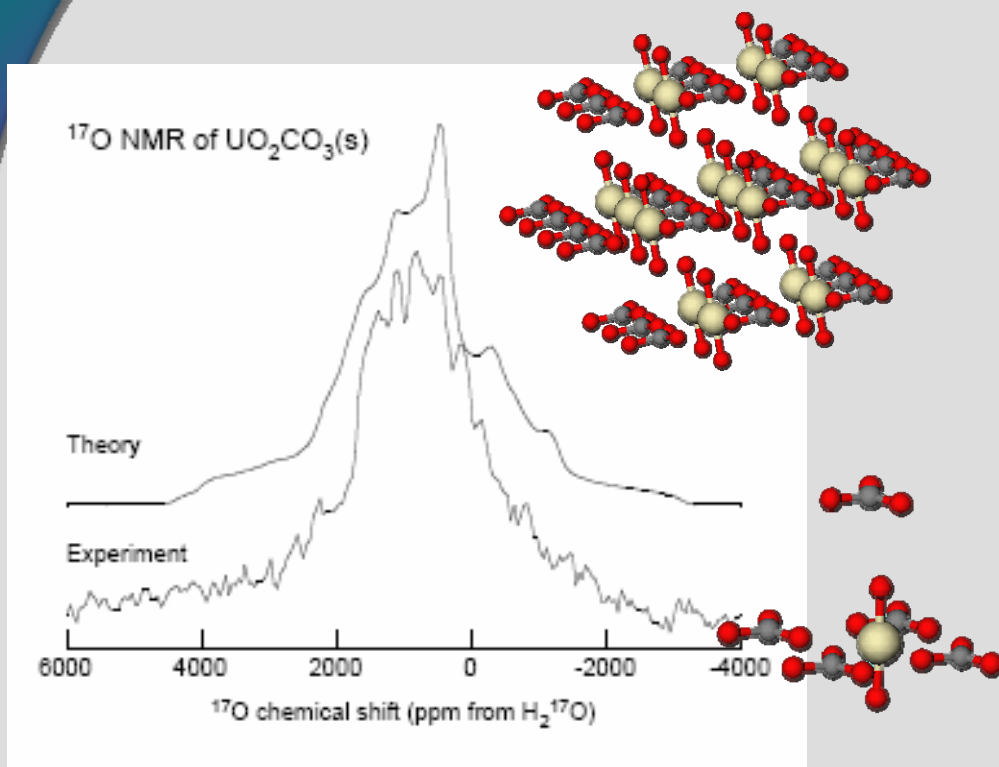
Temp (K)	Gas phase	Cosmo	Experiment
283	-120.29	-131.24	132.5 ( $\pm 0.2$ )
293	-120.24	-131.18	132.1 ( $\pm 0.1$ )
318	-120.10	-131.03	131.9 ( $\pm 0.1$ )

- ▶ Temperature dependence is much smaller
- ▶ Modeling results match with experimental data
- ▶ Calculations predict isotope dependence in the order of 0.01 Hz
- ▶ Dependence too small to be measured experimentally

# Predicting and Interpreting NMR Properties in Actinide Complexes

## Uranium-Oxide Research:

- NMR could be used for speciation of uranium complexes in nuclear waste tanks
- Computational Modeling guides experiments
- Calculations predict highly unusual spectrum
- Subsequent experimental result in good agreement with experiment



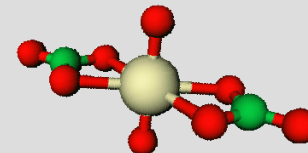
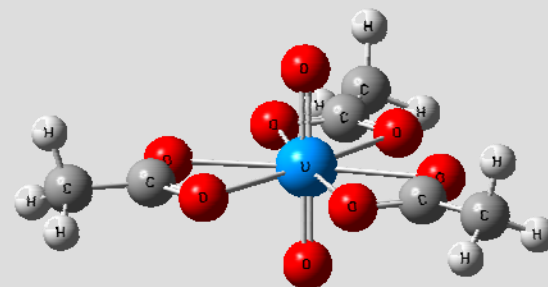
***Record anisotropy predicted and measured***

## Collaborative Research

Modeling: Bert de Jong (EMSL@PNNL)  
 NMR measurement: Herman Cho (PNNL)  
 Synthesis: John Abrefah a.o. (PNNL)

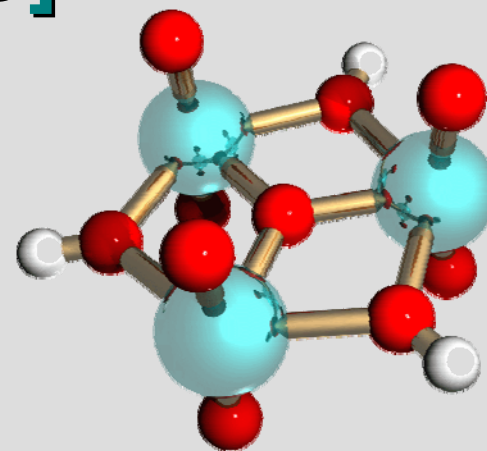
# Approach used successfully for uranyl carbonate, nitrate, and acetate complexes

- ▶ Understanding uranyl complex formation is vital for Hanford remediation efforts
- ▶ Comprehensive and systematic study
  - $\text{UO}_2^{2+}\text{X}_n$  with  $\text{X}=\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{CO}_2^-$ , and  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$
  - Geometries, spectroscopy, energetics (relative stabilities)
- ▶ Collaborative effort by
  - de Jong, Apra, Windus (PNNL)
  - Nichols, Harrison (ORNL)
  - Gutowski, Dixon (Univ. Alabama)
- ▶ In Press: J. Phys. Chem. A (2005)



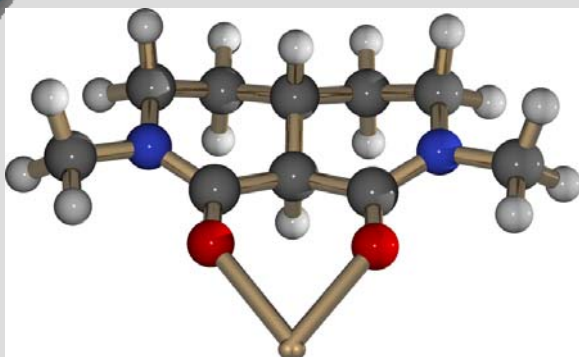
# Structure and NMR of $[(\text{UO}_2)_3(\text{OH})_3\text{O}]^+$

- ▶ Key compound in sol-gel processes relevant to nuclear fuel production
- ▶ Studied experimentally
  - NMR data still unresolved
- ▶ Collaboration with Dave Dixon (Univ. Alabama)
- ▶ Modeling of free ion and ligands (HMTA) attached:
  - Structure
  - Vibration
  - NMR chemical shifts (central oxygen)

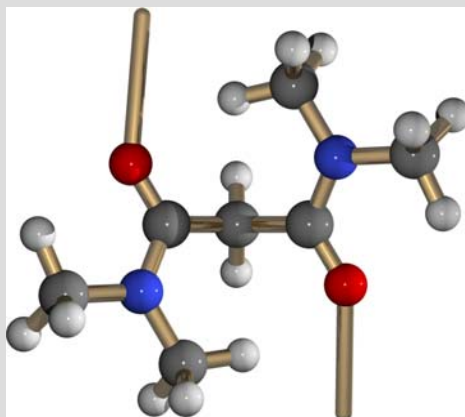




# Deliberate design of ligand architecture yields dramatic enhancement of metal ion affinity



computer-designed structure



conventional structure

Theoretical study of malonamides determines the optimum structure for heavy-metal binding,

Pacific Northwest National Lab and University of Oregon researchers designed a bicyclic architecture that locks in the optimal orientation of the carbonyl groups.

Synthesize novel ligands

Measure the organic/aqueous solvent distribution coefficient of one of the bicyclic compounds for chelating  $\text{Eu}^{3+}$  ions and drew them into the organic phase.

Improvement in binding of the bicyclic ligand by seven orders of magnitude over the best acyclic malonamide.

“Designer bindings”, Editors’ Choice article in *Science Magazine* **2002**, 296, 985.

“Designed ligands boost metal binding”, Science Concentrate article in *Chemical and Engineering News* **2002**, 80(20), 37.

**Battelle**

*J. Am. Chem. Soc.*, **2002**, 124, 5644

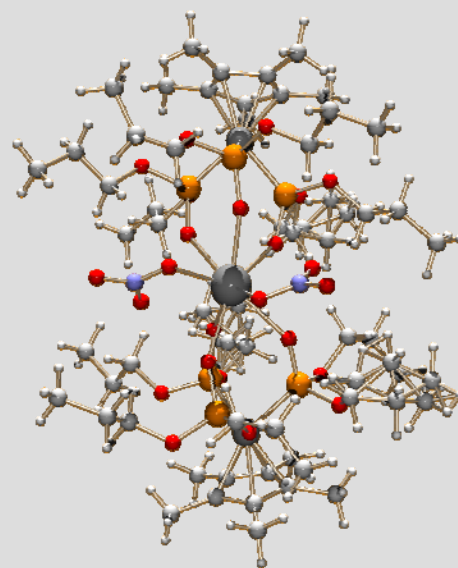
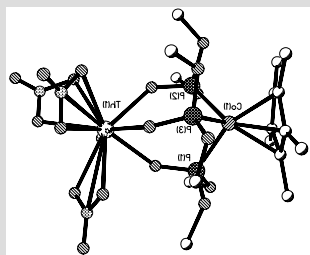
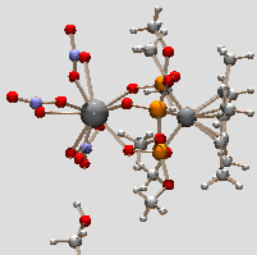
Gregg J. Lumetta, Brian M. Rapko, Pricilla A. Garza, and Benjamin P. Hay\*  
*Pacific Northwest National Laboratory*

Robert D. Gilbertson, Timothy J. R. Weakley, and James E. Hutchison\*  
*Department of Chemistry, University of Oregon*

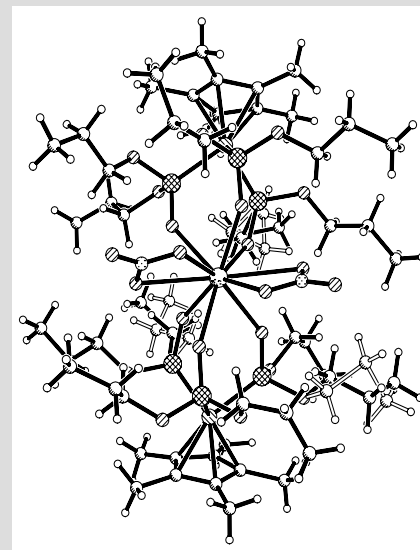
**Pacific Northwest National Laboratory**  
**U.S. Department of Energy**

# Kläui ligands for actinide separation

- ▶ Kläui ligand has potential to be selective actinide extractant
- ▶ Collaboration with experimentalists at PNNL
- ▶ Experiments with various functionalized Kläui ligands
  - IR spectroscopy
  - NMR spectroscopy



*Experiment*

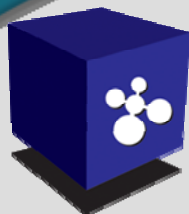


*Modeling*

- ▶ Structure and vibrational modeling done by Jun Li (PNNL)

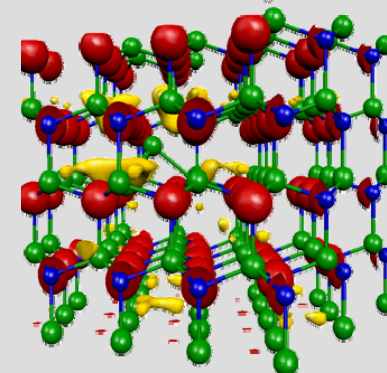
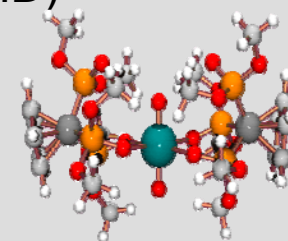
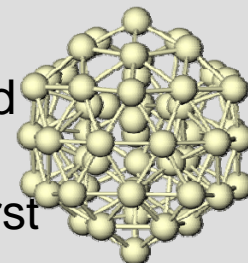
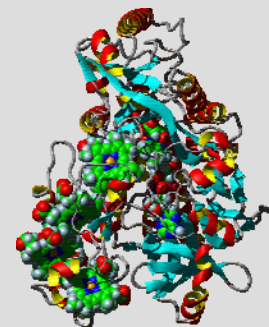
## Acknowledgement

- ▶ This research was performed in part using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory, operated for the Department of Energy by Battelle.
- ▶ Part of this research was funded under PNNL Level VI Laboratory Directed Research and Development (LDRD)

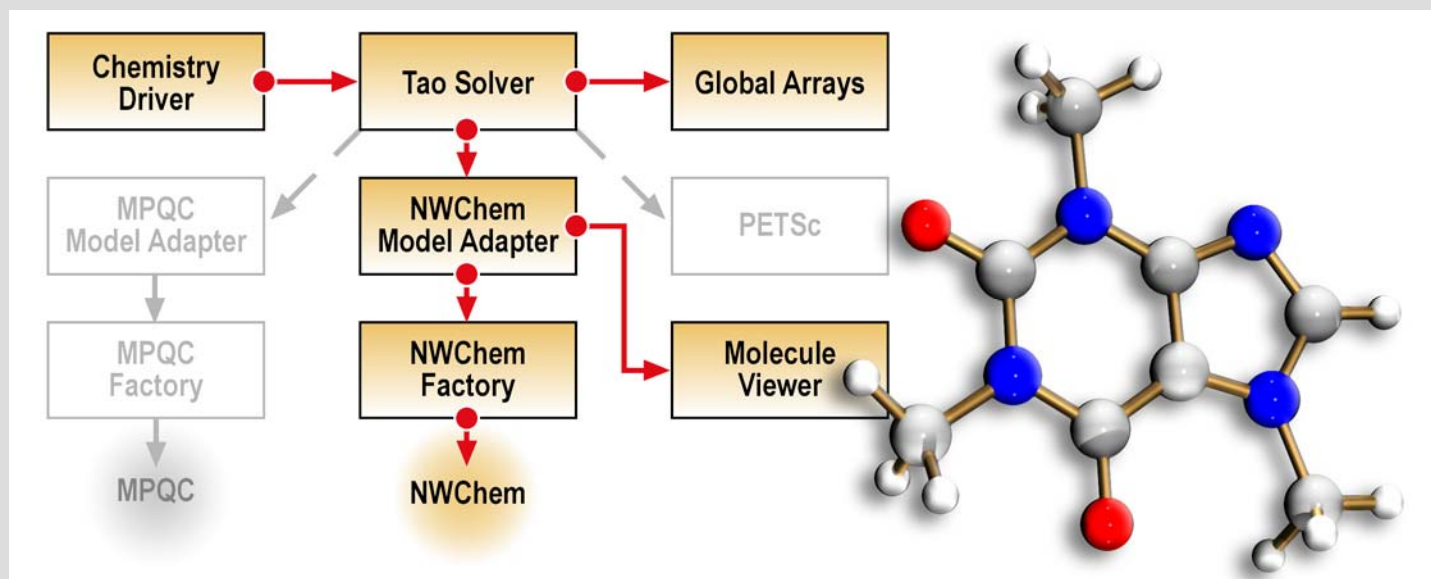


# NWChem Overview

- ▶ Provides major modeling and simulation capability for molecular science
  - Broad range of **molecules**, including **biomolecules**, **nanoparticles** and heavy elements
  - Electronic structure of molecules (non-relativistic, relativistic, ECPs, first and second derivatives)
  - Increasingly extensive **solid state** capability (DFT plane-wave, CPMD)
  - Molecular dynamics, molecular mechanics
- ▶ Emphasis on modularity and portability.
- ▶ Freely distributed (downloaded by 502 research groups in the last 12 months)
- ▶ Performance characteristics – designed for MPP
  - Single node performance comparable to best serial codes
  - Scalability to 1000's of processors
- ▶ Portable – runs on a wide range of computers

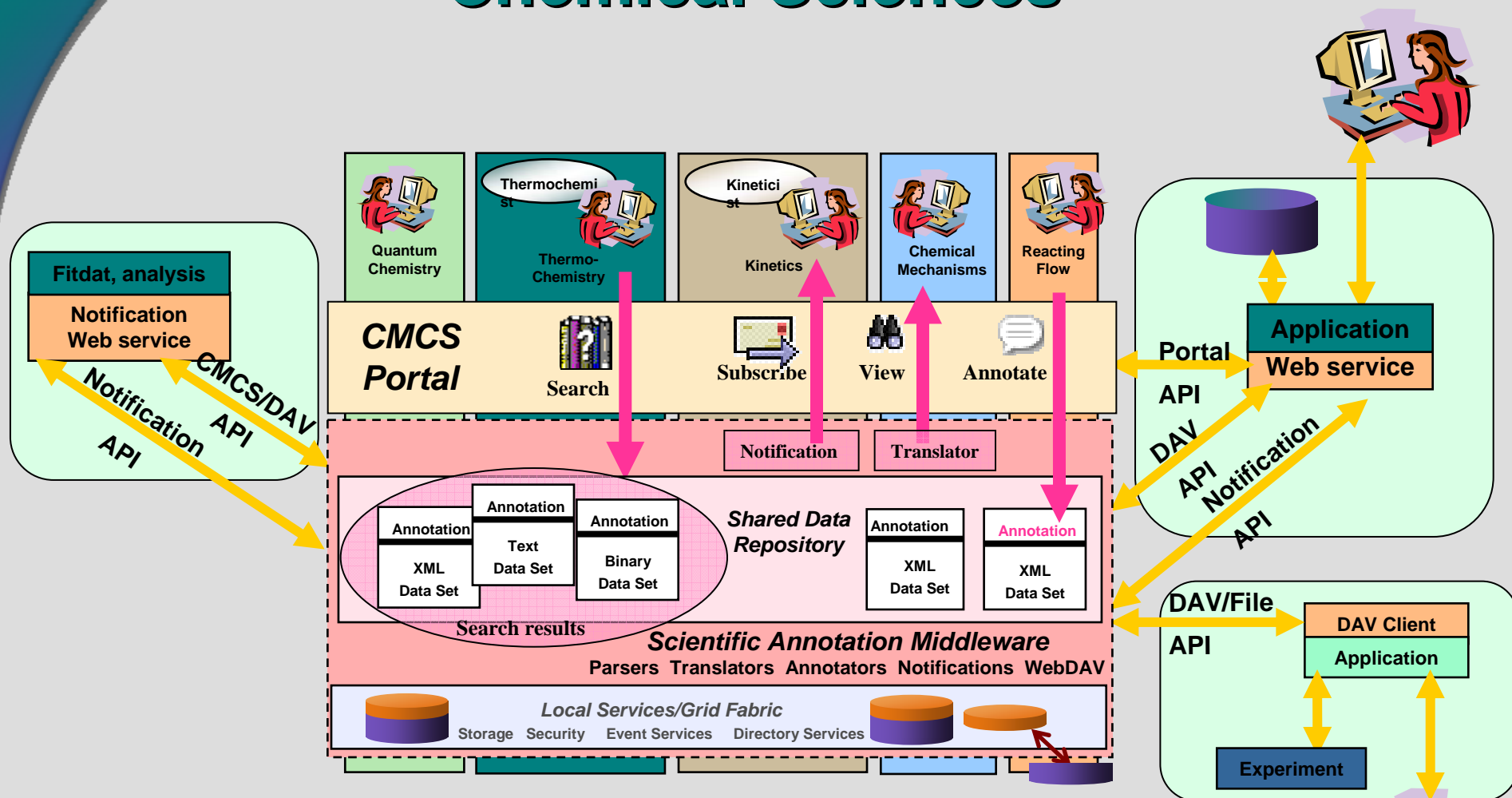


# Common Component Architecture



Needed to define a common interface for MPQC and NWChem as well as for PETSc and GA

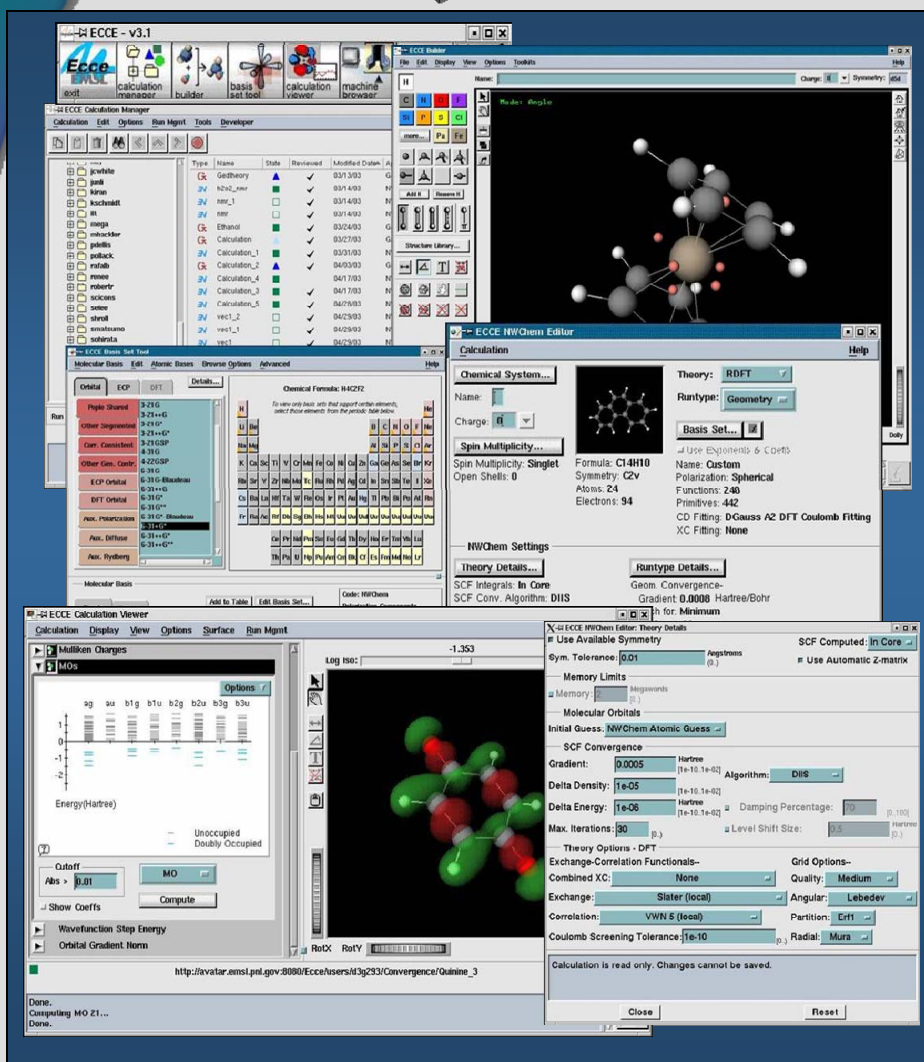
# Collaboratory for Multi-scale Chemical Sciences







# Ecce



- A comprehensive problem-solving environment (PSE) for molecular modeling and simulation. Key components include:
- Rich graphical user interface applications tightly integrated with message passing
- Flexible, high performance web server based data management for user computational studies
- Transparent support for running jobs on workstations, clusters, and supercomputers using industry standard remote communications
- Live monitoring and visualization of multi-dimensional properties— orbitals, normal modes, etc.
- Code registration framework
- Extensive web-based help